Magnetically stabilized luminescent excitations in hexagonal boron nitride

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Abstract

Magnetically stabilized luminescence is observed in hexagonal boron nitride. The luminescence is induced by absorption of cold neutrons and is in the visible region. In the absence of a magnetic field, the photon emission level is observed to decay over several hundred seconds. A fraction of this luminescence can be suppressed if the temperature is $T \lesssim 0.6\,\mathrm{K}$ and the magnetic field is $B \gtrsim 1.0\,\mathrm{T}$. Subsequent to irradiation and suppression, luminescence can be induced by an increase in T or lowering of B. Possible explanations include stabilization of triplet states or the localization and stabilization of excitons. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The study of luminescence in hexagonal boron nitride (h-BN) brings to light properties intrinsic to the material as well as its defects and impurities. Techniques used to study h-BN include electron paramagnetic resonance [1,2], thermally stimulated luminescence [3], thermally stimulated conduction [3], and luminescence induced by light, cathodic, electric, ionic, and radioactive sources [4–7]. Identified defects include F-centers, nitrogen vacancies and elemental impurities [6,8–12]. In-

formation about the intrinsic nature of h-BN has been obtained through studies of the near-band-gap luminescence [13].

A continuum photon emission spectrum in h-BN has been observed as a result of thermal neutron exposure which produces energetic $\mathrm{He^+}$ (1.47 MeV) and $^7\mathrm{Li^+}$ (0.84 MeV) ions in the material via the $^{10}\mathrm{B}(n,\alpha)^7\mathrm{Li}$ reaction. Other irradiation studies used 1.0 MeV $\mathrm{H^+}$ and 1.8 MeV $\mathrm{He^+}$ ions and resulted in the characterization of a continuum photon emission spectrum of 280–600 nm [7]. Here we present observations of magnetic suppression of cold neutron induced luminescence in h-BN at low temperature. The luminescence is stimulated by the by-products

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of neutron capture and can be suppressed by application of a magnetic field. The studies we present here were prompted by the use of h-BN as a neutron shielding material in an experiment to magnetically trap ultracold neutrons (UCN) [14].

2. Experimental apparatus

Hexagonal boron nitride is used in our neutron trapping apparatus to collimate an incident neutron beam and to absorb those neutrons scattered out of the collimated beam. Boron compounds are commonly used as shielding materials for absorbing low energy neutrons. Natural boron has a 19.9% abundance of ^{10}B, which has a large thermal neutron absorption cross section, $\sigma_{thermal} = 3840$ b. Hexagonal boron nitride is particularly suitable because of its high purity and mechanical properties. Hexagonal BN can be obtained with $<0.4\%$ oxygen and $<0.1\%$ all other total elemental impurities.[1] It is easily machinable and has a low thermal expansion coefficient. The h-BN used in our experiment is obtained commercially as a solid cylinder and machined into the form of interlocking tubular pieces with inner diameters of 3.86 cm and outer diameters of 4.16 cm. The assembled h-BN tube fits inside a cupronickel (CuNi) cell body and extends its entire length, 110 cm (see Fig. 1). Two cylindrical rings are used as neutron collimators and are positioned at distances of 36 and 74 cm relative to the front (beam entrance) of the h-BN tube. These rings each have an inner diameter of 2.0 cm, length of 1 cm and fit snugly within the h-BN tube. The cell is filled with liquid ^{4}He and is cooled by a dilution refrigerator from 1.0 to 0.1 K.

A cold neutron beam (moderated to 40 K) traverses the cell parallel to the long axis with a fluence of approximately 5×10^{8} s^{-1}. About 60% of the neutrons entering the cell are absorbed by the h-BN. A set of superconducting magnets
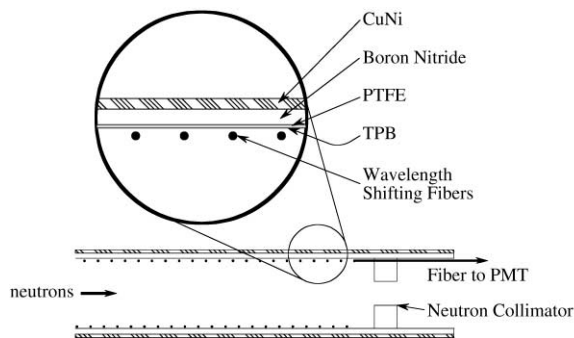

Fig. 1. Neutron shielding and light collection system. Neutrons enter from left, are collimated by a h-BN collimator, pass through the detection region and exit through a second collimator. The detection system consists of an expanded PTFE diffuse reflector with a thin layer of TPB evaporated onto the inner surface. The light is transported out of the apparatus using two helically coiled wavelength shifting fibers which are coupled into PMTs at room temperature.

resides just outside the cell body and when at maximum current, the h-BN is in a magnetic field ranging from 1.0 to 1.8 T.

Under normal operating conditions, a light collection system is situated just inside the tube of h-BN between the two collimators (see Fig. 1). This system consists of a diffuse reflector made of expanded polytetrafluoroethylene (PTFE) onto which is evaporated an ultraviolet-to-blue down-converter (tetraphenyl butadiene, TPB) [15] and two helically coiled blue-to-green wavelength shifting fibers.[2] The fibers exit the cryogenic apparatus and are each coupled to a photomultiplier tube. This system is sensitive to photons over the entire spectrum from the extreme ultraviolet (EUV; <100 nm) to the visible blue (~ 500 nm) and is not capable of further wavelength discrimination.[3]

3. Results

In a typical run, the detection region is exposed to neutrons for 900 s. During this irradiation

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[1] AX05 grade h-BN, Carborundum Inc., Amherst NY. Certain trade names and company products are mentioned in the text in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by NIST.

[2] Y11 scintillating fiber purchased from Kuraray Co., Ltd. 8F, Mauzen Building, 3-10, 2-Chome, Nihonbashi, Chuo-ku, Tokyo, 103-0027, Japan.

[3] The fiber light collection system was not actually used in the measurement made in Ref. [14].

period, the photomultiplier tubes (PMTs) are turned off. After 900 s, the neutron beam is blocked, the PMTs are brought up to voltage and luminescence is detected.

The time dependence of the luminescence signal is shown in Fig. 2 (solid line), starting at the point when the beam is turned off ($t = 0$ s). This decay does not fit to a single exponential and varies roughly as inverse time. When the magnet is energized during the irradiation and observation, a significant fraction of this luminescence signal is suppressed (see Fig. 2, dashed line). When the field is lowered (starting at 1275 s), luminescence from the "stored" component is emitted.

Numerous tests were performed to identify the source of the luminescence signal and to characterize its behavior. By the process of elimination using multiple experimental setups, we determined that the luminescence signal was originating from the boron nitride and simplified the detection system to verify this conclusion. In the experimental setup shown in Fig. 3, only h-BN and an acrylic lightguide were present (the TPB downconverter and wavelength-shifting fibers were removed), and the geometry was arranged such that neutrons could not directly impact the acrylic. The luminescence signal was observed. Both components of this decay

signal can be seen in Fig. 4. In separate tests performed at 4 K, we did not observe luminescence in an acrylic sample under similar neutron irradiation conditions.

Studies to characterize the behavior of the magnetically stabilized component of the luminescence signal were performed using the fiber cell apparatus (Fig. 1). Data resulting from lowering the magnetic field in various ways is shown in Fig. 5. The initial irradiation takes place with the magnets at maximum current. In Fig. 5A the magnet current is held constant for 800 s after the neutron beam is turned
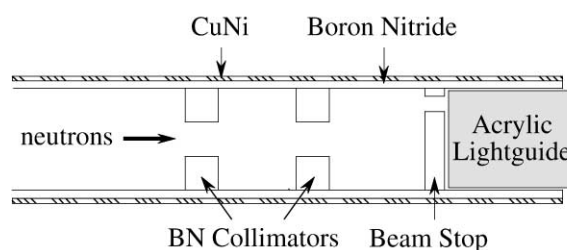

Fig. 3. Schematic diagram of the simplified apparatus used to verify the luminescence was originating from the boron nitride. The beam stop has three 4 mm slits machined at a radial distance of 14 mm from the center of the beam stop to allow the light to enter the acrylic lightguide. No unscattered neutrons can reach the acrylic lightguide.
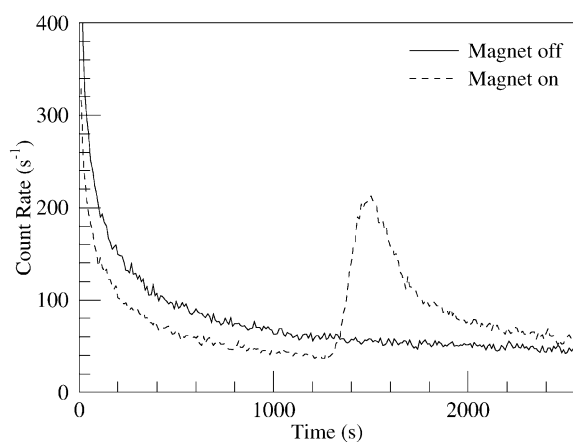

Fig. 2. The time dependence of the luminescence signal with no magnetic field (—) and when the magnetic field is energized during the irradiation and de-energized 1275 s after the irradiation ends. (- - - -)
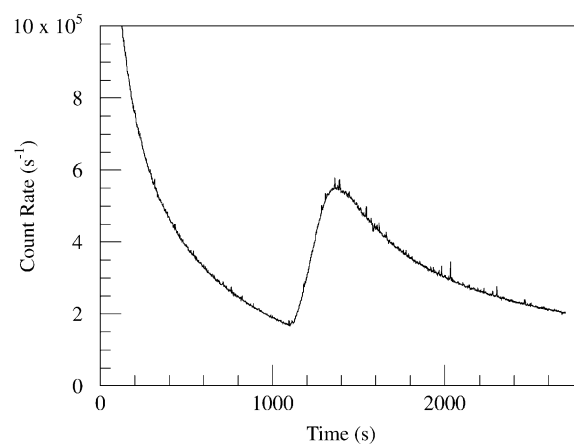

Fig. 4. Luminescence signal using the set up shown in Fig. 3. The magnetic field is energized during the irradiation and initial observation times and de-energized 1275 s after the irradiation ends.
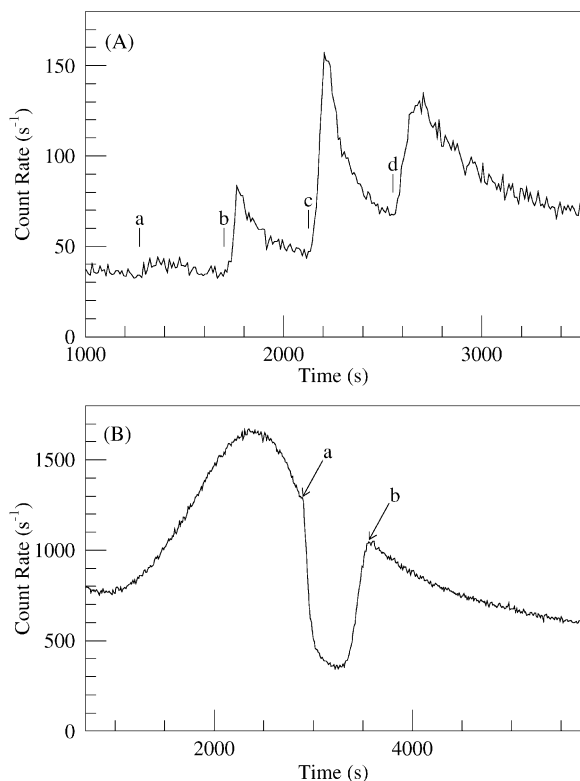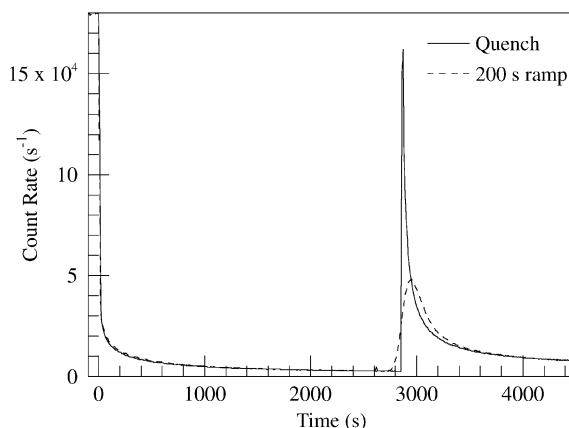
Fig. 6. The time dependence of the luminescence signal when the magnet is de-energized in less than 1 s (—) and the time dependence when the magnet is de-energized using a slower ramping speed of ≈ 200 s (- - - -).

Fig. 5. (A) The effect of lowering the magnetic field (B) in four steps as follows: (a) $t = 1275$ s, $B = 100\% \rightarrow 75\%$; (b) $t = 1700$ s, $B = 75\% \rightarrow 50\%$; (c) $t = 2125$ s, $B = 50\% \rightarrow 25\%$; (d) $t = 2550$ s, $B = 25\% \rightarrow 0\%$. (B) The magnetic field is slowly lowered from its initial maximum value to zero over 2700 s. Just after this ramp ends, the field is rapidly raised to its maximum value beginning at point "a" and 570 s later, the field is lowered back to zero (point "b").

off. Then the magnetic field is reduced in four steps: from $100\% \rightarrow 75\%$, $75\% \rightarrow 50\%$, $50\% \rightarrow 25\%$ and $25\% \rightarrow 0\%$ of its maximum value. The largest fraction of the luminescence is emitted in the last two reduction steps. Fig. 5B further demonstrates the suppression of luminescent emission. In this measurement, the magnetic field is slowly ramped down from 100% to zero over 2700 s. Immediately after this, the field is rapidly (~ 100 s) turned back to 100% for 570 s and then back to zero. As can be seen, the luminescence is suppressed while the field is on. We have verified, in a separate experiment, that the magnetic field has no

significant effect on the efficiency of the detection system.

To characterize the time dependence of the decay of the stabilized component, the superconducting magnet was quenched resulting in a reduction in field from its maximum value to zero in less than 1 s. The time dependence of this decay signal is roughly the same as the initial decay (see Fig. 6). In addition, the total integrated number of counts using the magnet quench signal is roughly equal to that obtained using a slow field ramp. Presumably the luminescence is the result of relaxation of some type of solid state excitation in the h-BN.

The persistence of these excitations under conditions of high magnetic field is most dramatically demonstrated by leaving the magnetic field on for 28 800 s after irradiation. After this time the magnetic field is lowered to zero and luminescence is observed. The number of photons emitted after 28 800 s was within 50% of the number emitted after only 1000 s of storage (under the same irradiation conditions).

We also observed that raising the temperature of the cell has a similar effect to lowering the magnetic field. Fig. 7 shows data for different field and temperature conditions. In both sets of data, the cell was irradiated by the neutron beam for 900 s. In Fig. 7A, the magnetic
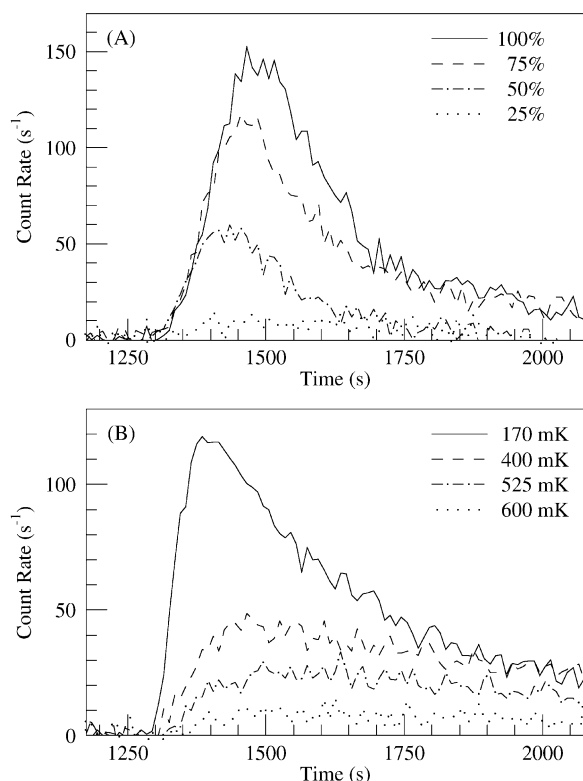
Fig. 7. (A) The change in intensity of the luminescence signal due to variation of the magnitude of the magnetic field. Each trace is for a different initial magnetic field intensity. In each case the magnet is brought from its initial value to zero in 100 s. (B) The change in intensity of the luminescence signal due to varying the temperature of the cell. Each trace is for a different initial temperature. In each case the temperature is raised from its initial value to 1 K while the magnet is kept at 100% of its full value.

field is lowered from its initial value to zero in approximately 100 s beginning 1275 s after the beam is turned off. Traces are shown for initial magnet currents of 100%, 75%, 50% and 25% of its maximum current. The data shown in Fig. 7B are taken maintaining the magnet at its maximum current while raising the temperature of the cell from its initial value to 1 K in approximately 100 s beginning 1275 s after the beam is turned off. The traces are for initial temperatures of 170, 400, 525 and 650 mK. It is important to note that temperature changes brought about by eddy current heating while ramping the magnetic field (< 20 mK) are much

smaller than those required to initiate the release of luminescence (> 200 mK).

4. Discussion

Given the myriad of mechanisms for producing luminescence, we can only offer general hypotheses about the magnetically stabilized component of the luminescence signal and offer some general points. The energy of interaction of the magnetic moment of an electron or hole in h-BN with a magnetic field of 1 T in temperature (Kelvin) units is 1.3 K. This is the same energy scale as that observed in Fig. 7. Our highest applied field of 1.8 T results in an energy of interaction ~ 2.3 K. The applied magnetic field should lead to polarization of paramagnetic species as the thermal fluctuations present in the solid are not energetic enough for depolarization. In addition to electrons and holes, other possibilities for paramagnetic species present in the h-BN include triplet state excitons. These typically have a magnetic moment of one Bohr magneton ($1\mu_{B}$) or greater. Spin polarization of trapped electrons, holes or excitons may take place and then affect the possible relaxation paths to luminescence.

One possibility is that the magnetic field stabilizes a triplet state of a defect center such as an F-center. Triplet states can have very long lifetimes [16] and the stabilization would prevent conversion to the much shorter lived singlet state. Observations of magnetic suppression of singlet-state formation, resulting in enhanced triplet state formation has been observed in alkali halides [17,18]. Unlike our case, these triplet states exhibit pure exponential decay which is uneffected by magnetic field changes. Another possibility is that the interaction of an electron or exciton with a paramagnetic center causes trapping, similar to that seen in indium antimonide [19]. The applied magnetic field could keep the two species aligned. As the temperature is raised (or the field lowered) thermal fluctuations would release the excitations which could then undergo radiative recombination. The apparent distribution of trapping energies may indicate a combination of

thermoluminescent activity with a magnetic interaction. That is, the usual thermoluminescent trapping is modified by some type of magnetic interaction, perhaps one of those discussed above. In this case, the spatially varying magnetic field would provide a continuum of trapping energies.

5. Conclusion

We have observed a magnetically stabilized component in the luminescence of h-BN under neutron irradiation. The excitations that give rise to the luminescence can be stabilized for long periods by high magnetic fields ($\approx 1\,\mathrm{T}$) at low temperatures ($\lesssim 600\,\mathrm{mK}$). Further experiments are necessary to elucidate the nature of the excitations, including spectroscopic analysis of the luminescence, quantitative analysis of the magnetic field dependence and optically detected electron paramagnetic resonance.

Acknowledgements

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